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C-14 REMOVAL FROM SPENT IX RESINS
PHASE I - LABORATORY EVALUATION OF METHODS

Report No. 88-120-K

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ABSTRACT

Several methods for removing C-14 from spent resins have been evaluated experimentally with simulated spent resin samples. C-14 removal by reacting spent resin with acid in an agitated batch reactor was shown to be highly effective. Based on laboratory experiments with simulated moderator spent resin, a recovery efficiency between 98.5% and 100% can be claimed for this method with a level of statistical significance at 90-95%. Preliminary assessment also indicates that the amount of secondary wastes to be generated by this process would not be excessive and should not offset the potential benefits. Continued laboratory work with actual moderator spent resin and a pilot plant study have been recommended.

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EXECUTIVE SUMMARY

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In nuclear reactors, carbon-14 (C-14) is formed mainly by neutron activation of oxygen-17 and nitrogen-14, and is a radioactive contaminant that should not be released to the environment. The bulk of C-14 production in CANDU reactors occurs in the moderator water and the primary coolant. The C-14 formed is largely removed by ion exchangers in the respective purification circuits: 90-95% of the C-14 in moderator water is removed and fixed on moderator ion exchange resin, and about 98% of that in the primary heat transport (PHT) system is removed by PHT resin. Carbon-14 has a long half-life of 5730 years and its presence on these resins (at levels around 47-213 Ci/m^3 for moderator spent resin and 0.8-5.6 Ci/m^3 for PHT spent resin) makes direct disposal of the low- and intermediate-level radioactive resin wastes difficult. The removal and isolation of C-14 from the bulk resin waste may provide economic and technical advantages for resin disposal, and also the potential for marketing it as a commercial source of C-14 isotope. A program was therefore initiated in 1987 to develop a process in which C-14 could be effectively removed from the spent resins.

This first phase of the program consisted of a survey of the previous studies and laboratory evaluation of several selected spent resin treatment methods.

The previous work included a gas displacement method, which was tested at 25°C and 70°C by flushing the resin with air or air enriched with 10% CO_2. The C-14 removed from the resin ranged from 22% to 63% with one peak performance showing practically 100% removal. A thermal stripping method was also attempted where the resin was heated to 170-200°C with oxygen or

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nitrogen as carrier gas, and high C-14 recoveries (93-98%) were obtained for simulated spent resin. With actual spent resin, only 21-24% of C-14 was removed. Different methods of acid stripping were also attempted previously, and the results ranged from 14% by simply heating with acid, to 62-96% by fluidizing a resin column with HCl, and to 92-100% by vibrating the resin with an ultrasonic probe in acid-fluidized column. However, the consistency of the previous results was difficult to determine because only limited data had been reported.

This study concentrated on the method of acid stripping by reacting the resin with HCl in an agitated batch reactor. Other reagents such as NaCl, Na_2CO_3 and NaOH have also been briefly tested, but the results were not promising. The experiments of acid-stripping the simulated spent resins with HCl were also repeated sufficiently to verify statistically the consistency of the performance, and a recovery efficiency of 98.5-100% could be claimed with reasonably high levels of statistical significance (95% for Type I error, 90% for Type II error). A few selected samples of stripped resins were analyzed and the resins were found to be practically free of residual C-14.

A preliminary assessment indicates that the total amount of waste by-products such as the spent acid and caustic generated during this process would be about 30 mL for each 100 mL of resins processed.

It is recommended that the method of acid stripping by agitation should be further developed for plant application. Additional work has been planned to test the performance with actual spent resins and then to scale up the operation to pilot-plant size for an in-depth technical evaluation.

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C-14 REMOVAL FROM SPENT IX RESINS
PHASE I - LABORATORY EVALUATION OF METHODS

1.0 INTRODUCTION

The emission of radioactive carbon-14 (C-14) from nuclear stations should be minimized to avoid the possibilities of its becoming a health hazard. Carbon-14 has a long half-life of 5730 years, and it can cause radiation dosage to inhabitants by contact, inhalation or through the food cycle via photosynthesis. In nuclear reactors, C-14 is formed mainly by neutron activation of oxygen-17 and nitrogen-14, and to a negligible extent, carbon-13. Most of the C-14 production in CANDU reactors occurs in the moderator and the primary coolant: and the C-14 formed is effectively removed by the ion exchangers in the respective purification circuits. Approximately 90 to 95% of the C-14 in the moderator water is removed by moderator resin, and about 98% of that in the primary coolant is removed by the primary heat transport (PHT) resin. The levels of C-14 on the resins are about 47-213 Ci/m^3 of moderator spent resin and 0.8-5.6 Ci/m^3 of PHT resin/1,2/. The presence of C-14 makes direct disposal of the low- and intermediate-level radioactive spent resins difficult. The removal and isolation of C-14 from the bulk resin wastes may provide significant economic and technical advantages for resin disposal and also the marketing potential of C-14 isotope/3/. A program was initiated in 1987 to develop a process which may effectively remove C-14 from the spent resins and reduce radioactive waste volumes without creating secondary waste problems.

Figure 1 is a conceptual flowsheet for the envisaged process. The spent resin is first treated by a suitable stripping chemical until the C-14 is sufficiently removed and the resin is suitable for disposal as low- or intermediate-level radioactive waste. The C-14 removed is first transformed into gaseous $^{14}CO_2$ and then absorbed or adsorbed by a suitable sorbent. The off-gas is finally discharged to the atmosphere. The spent sorbent and the spent chemical are the secondary wastes which may require proper treatment before final disposal.

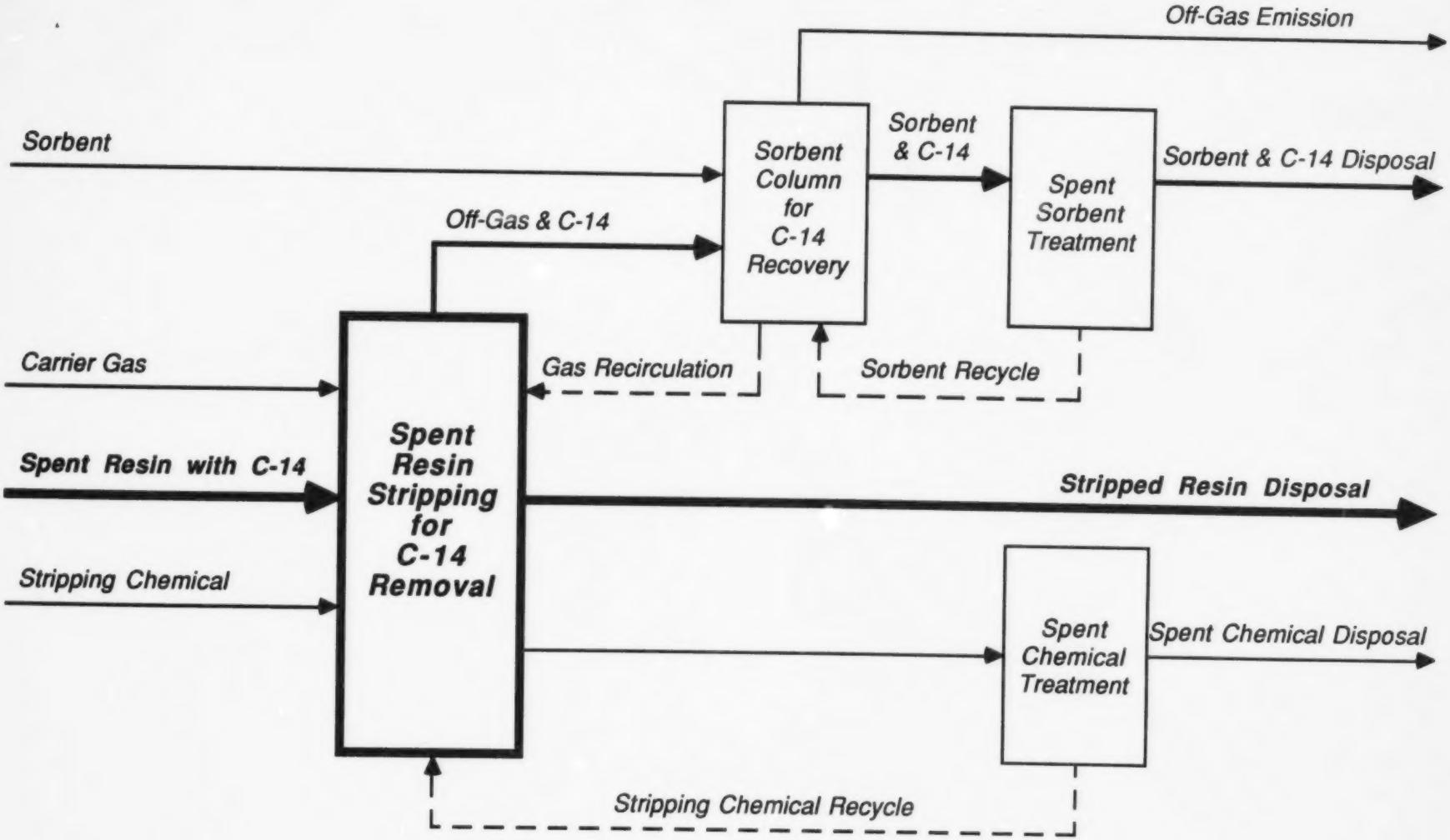

FIGURE 1

CONCEPTUAL FLOWSHEET FOR SPENT RESIN PROCESSING

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This study represents the first phase of the program and includes a survey of the previous results, laboratory evaluation (with simulated spent resins) of several chemical stripping techniques and a preliminary assessment of the extent of secondary waste generation. Subsequent phases of the program will include experimentation with actual spent resins, a more detailed assessment of secondary wastes, and a pilot plant evaluation.

Several resin treatment methods for C-14 removal have been tested in previous studies. The gas displacement method was tested by Buckley/4/ at two different temperatures, 25°C and 70°C, by flushing the resin with a carrier gas. When air was used as carrier gas, the removal of C-14 from the resin was negligible, but when the carrier gas was enriched with 10% CO_2, the removal efficiencies improved to 22-63% with one peak performance at practically 100%. Bonnici et al/5/ tested the thermal stripping method by passing oxygen or nitrogen over simulated spent resins maintained at elevated temperatures (170-200°C) and obtained high removal efficiencies (93-98%). Performance of the same technique with an actual moderator spent resin sample was, however, unsatisfactory with only 21-24% C-14 removal. Bonnici et al/5/ also attempted one trial with acid stripping by heating a small sample of moderator spent resin with 2N HCl at 90°C for two hours but achieved only 14% C-14 removal. The acid stripping method was conceived and studied in detail by Nott/6,7,8/. The initial tests of an acid fluidized resin column showed 62-96% recovery of C-14 from simulated spent resin. The apparatus was later modified by adding an ultrasonic probe to intermittently vibrate the resin beads within the fluidized column, and the recovery was improved to 92-100%. These results are included in Appendix A for reference.

The present work included some exploratory laboratory experimentation of several resin treatment methods and a detailed investigation of the technique of acid stripping in an agitated batch reactor. Some preliminary tests of the effectiveness of $Ca(OH)_2$ solid sorbents for removing $^{14}CO_2$ from the off-gas stream were also conducted.

2.0 EXPERIMENTAL

A stock solution of known radioactivity was first prepared by diluting C-14 labelled Na_2CO_3 or $NaHCO_3$ (supplied by NEN/Du Pont and Amersham) with deionized water. Simulated spent resins were then prepared by equilibrating a known amount of fresh resin with a known amount of activity withdrawn from the stock solution. The loading of activity on the resins was determined by liquid scintillation counting (LSC) of the solution before and after equilibration. For reasons to be explained later (Sec. 3.1), except for a few initial experiments, all samples were counted in 2N NaOH with addition of Hionic scintillation cocktail (supplied by Canberra-Packard). About 50 Ci/m^3 of C-14 was loaded on Amberlite IRN 150 resin to simulate moderator spent resin, and 5 Ci/m^3 on IRN 154 to simulate spent PHT resin.

A sketch of the experimental apparatus is shown in Figure 2. The C-14 loaded resin is mixed with a stripping solution (HCl, NaCl, Na_2CO_3, or NaOH depending on the experiment) in a glass flask and the slurry is agitated by a magnetic stirrer. Air sparging at an average rate of 135-150 mL/min was applied to purge any CO_2 generated, and to carry the off-gas through a water trap (acidified with 5% acid) and two absorber traps containing liquid sorbents. Sodium hydroxide solutions (2N NaOH) were used as sorbents in most of the runs except in a few initial runs where the analytical chemical, Carbosorb (Canberra-Packard) was used. In three of the experimental runs, one-inch glass columns containing $Ca(OH)_2$ (88.6% pure, bulk density=0.43 g/mL) were used for sorption of gaseous CO_2. A vacuum pump was used for maintaining a slight negative pressure within the system, and for drawing the off-gas through the sorbents.

The method of acid-stripping in a fluidized column was tested in an apparatus similar to that shown in Figure A of Appendix A, with the exception that the ultrasonic vibration probe was deleted.

The efficiency of each technique was measured by the total C-14 activity recovered in the off-gas absorber as a percentage of the activity initially loaded on the resin, and it is dependent upon the efficiency of removing the C-14 from the resin as well as that of recovering it from the off-gas.

3.0 RESULTS AND DISCUSSION

3.1 Preliminary Experiments

The initial results obtained from acid stripping of simulated PHT spent resins in an agitated batch reactor were not consistent enough to be analyzed meaningfully. The data are summarized in Appendix B (Tables B-1, B-2), and a brief discussion is presented.

There was wide scatter in these initial results, and several measurements showed recoveries significantly in excess of 100% (8 runs in Appendix B showed recoveries ranging from 109 to 149%). It was not possible to determine the effect of the operating variables on C-14 recovery, due to the wide scatter in the data. The experimental results obtained according to a Plackett-Burman experimental design/10/ with four independent variables are summarized in Table 1 for the discussion. As can be seen from Table 1, the values of the F-statistic in the analysis of variance are such that the probabilities, P(>F), of erroneously assigning significance to the model and to the parameters are very high.

The cause of the inconsistencies in the data was investigated, and it was postulated that the solutions used in the off-gas absorbers and the LSC procedure for these initial experiments might have introduced discrepancies in the counting efficiencies. The aqueous samples (stock solution, resin

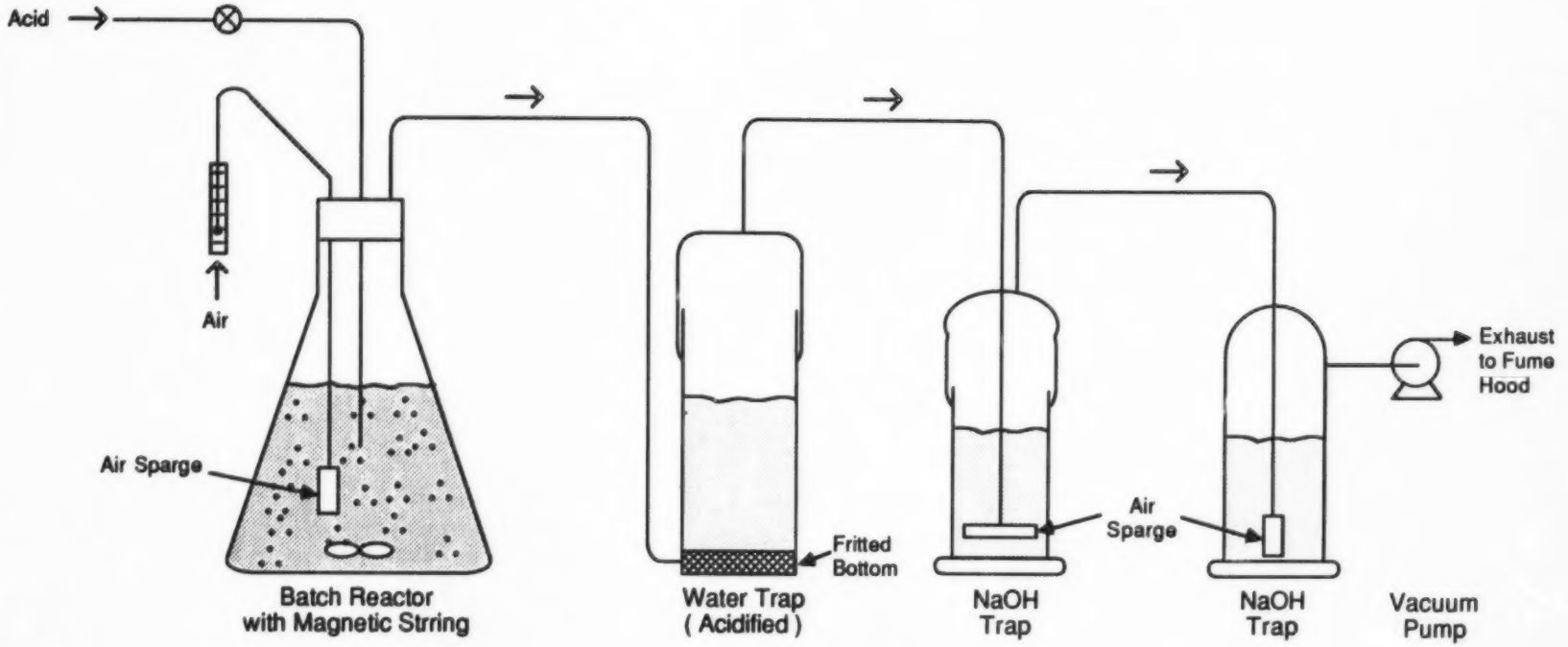

FIGURE 2. Apparatus for C-14 Removal by Agitation

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TABLE 1

Experimental Design and Analysis of Simulated PHT Spent Resin
(Plackett-Burman Design)

Experimental Data (30 mL of IRN 154 Resin with 5 Ci/m^3 C-14 loading)

RUN NO. (Ref. Table B-2)	ACID CONC. (N)	ACID VOL. (mL)	REACTION TIME (min)	AGITATION SPEED (rpm)	C-14 RECOVERY (%)
P-7	3	360	45	60	102.4
P-8	3	480	45	30	103.0
P-9	3	480	90	30	109.4
P-10	3	360	90	60	113.5
P-11	1	480	90	60	98.7
P-12	1	480	45	60	109.8
P-13	1	360	90	30	112.1
P-14	1	360	45	30	98.1

Analysis of Variance

Overall mean C-14 recovery = 105.9%

SOURCE	F-VALUE	PROBABILITY (>F)
Model	0.27	0.88
Acid Concentration	0.18	0.70
Acid Volume	0.05	0.83
Reaction Time	0.82	0.43
Agitation Speed	0.01	0.94

equilibration solution etc.) analyzed for these initial experiments were prepared in NaOH solution and mixed with PCS II (Phase Combining System II supplied by Canberra-Packard) cocktail for LSC. After acid stripping, the $^{14}CO_2$ evolved was absorbed in a commercial absorbent, Carbosorb, and counted with Permafluor cocktail (supplied by Canberra-Packard). When samples are prepared with different cocktails (eg. PCS II vs Permafluor) in different counting media (eg. NaOH vs Carbosorb), the counting efficiencies would be different. The sensitivity of C-14 determinations to changes in background conditions such as NaOH concentrations in PCS counting cocktail was investigated by Greening/9/, but similar studies for Carbosorb or other systems have not been conducted. In subsequent work, it was decided to eliminate the use of Carbosorb and count all samples in 2N NaOH medium with Hionic scintillation cocktail. Since the C-14 recovery was determined by the difference in the C-14 measurements of samples collected before and after acid stripping, any 'offsets' in counting efficiencies would cancel out provided that the differences in the sample background conditions (eg. chemical speciation, alkalinity, formulation of LSC cocktail etc) were minimized.

The results shown in Table 2 were obtained with the revised procedure for a set of experiments performed with simulated moderator spent resin according to a Plackett-Burman experimental design with four independent variables. None of the recovery data exceeded 100% and the results were more amenable to statistical analysis. The analysis of variance in Table 2 shows that the recovery efficiency was dependent upon a model consisting of the following four basic operating parameters: acid concentration, acid volume, reaction time and agitation speed; but the values of P(>F) for the individual parameters (ranging from 0.03 to 0.07) were not different enough to single out any particularly dominating parametric effects.

For improved consistency in LSC measurements, in all subsequent experiments the commercial chemical Carbosorb was replaced by 2N NaOH solution as the off-gas absorbent, and all samples for LSC were prepared in 2N NaOH medium for maintaining a uniform background condition. The efficiencies of the different resin stripping techniques were explored next and the detailed parametric studies were postponed until the selection of a suitable method could be finalized.

3.2 Evaluation of Resin Stripping Techniques

The results of the initial tests of the different techniques are presented in Table 3.

TABLE 2

Experimental Design and Analysis of Simulated Moderator Spent Resin
(Plackett-Burman Design)

Experimental Data (30 mL of IRN 150 Resin with 50 Ci/m^3 C-14 loading)

RUN NO.	ACID CONC. (N)	ACID VOL. (mL)	REACTION TIME (min)	AGITATION SPEED (rpm)	C-14 RECOVERY (%)
2-1	3	360	45	60	87.1
2-2	3	480	45	30	88.2
2-3	3	480	90	30	90.0
2-4	2	480	90	60	98.0
2-5	3	360	90	60	91.4
2-6	2	480	45	60	92.0
2-7	2	360	90	30	90.0
2-8	2	360	45	30	87.7

Analysis of Variance

Overall mean C-14 recovery = 90.6%

SOURCE	F-VALUE	PROBABILITY (>F)
Model	10.58	0.04
Acid Concentration	8.12	0.07
Acid Volume	9.66	0.05
Reaction Time	13.91	0.03
Agitation Speed	10.65	0.05

TABLE 3

Miscellaneous C-14 Removal Methods
(30mL of IRN 150 Resin with 50 Ci/m^3 C-14 loading)

RUN NO.	METHOD	REAGENT SOLUTION CONCENTRATION (N)	RUN TIME (min)	AGITATION SPEED (rpm)	AERATION RATE (mL/min)	SOLUTION VOLUME (mL)	PERCENTAGE C-14 RECOVERY (%)
1	Elution with Na_2CO_3	6	90	60	135	180	88.1
2	Elution with NaCl	6	90	60	135	180	19.3
3	Alkaline Stripping with NaOH	6	90	60	135	180	98.2
4(a)	Fluidization with HCL	3	90	-	400	480	93.9
4(b)	Fluidization with HCL	6	45	-	300	125	92.6
4(c)	Fluidization with HCL	6	90	-	0	125	96.8
4(d)	Fluidization with HCL	6	270	-	300	270	90.9

C-14 recovery by elution with Na_2CO_3 was 88%. Elution with NaCl resulted in only 19% recovery and alkaline stripping with NaOH yielded 98% recovery. C-14 recovery from acid stripping by fluidization ranged from 91 to 97%.

The mechanisms of elution and alkaline stripping are similar. The carbonate (or bicarbonate) on the resin is displaced by the anionic species, such as carbonate, chloride or hydroxide, in the solutions. The mechanism of acid stripping is one of chemical reaction where the acid reacts with the carbonate or bicarbonate on the resin evolving gaseous carbon dioxide.

During acid fluidization, air sparging was introduced in an attempt to improve the recovery efficiency by rapidly purging away the CO_2 gas formed on the resin beads. But contrary to expectation the efficiency of run 4(c)in Table 3 (without air sparging) was higher than those of other runs with air sparging. Upon examination, it was discovered that the air bubbles in the fluidized column tended to cause a 'shielding' effect upon the resin beads. The air bubbles were seen to adhere to and float with the resin beads in the fluidized bed, and thus probably reduced the contact and reaction between the resin and the acid. An increase in the rate of sparging did not free the bubbles from the resin beads, but rather caused some clogging of resin at the top of the column. Attempts to mechanically remove the air bubbles from the resin beads by agitation were quite successful, and detailed experiments were carried out to establish conditions for high C-14 removal.

The results of the experiments on the agitation method are summarized in Table 4. The first three runs (runs R-1, R-2, R-3) were repeats of a previous experiment, run 2-3 described in Table 2. The C-14 recovery was found to be around 90-92%, which confirms that the low efficiency noted in the previous run 2-3 was likely not erroneous.

Based on the results obtained in previous runs 2-4, 2-5 presented in Table 2, and those of runs S-1, S-2 and S-3 to be discussed later in Table 7 of section 4.0, the conditions employed for run E-1 were: high acid concentration (9N), low acid volume (90 mL), short reaction time (45 minutes, which can be simply prolonged to 90 minutes if required) and high agitation speed (60 rpm). After completion of experiment, the results of run E-1 were assessed in conjunction with all the previous results to determine the conditions for the next experiment run E-2. This sequential approach usually requires fewer number of experiments than the routine experimental design. The results in Table 4 quickly led to a high overall recovery close to 100% when the conditions of run E-3 (6N acid concentration, 135 mL acid volume, 45 minutes reaction time, 60 rpm agitation speed) were employed.

TABLE 4

Acid Stripping with Mechanical Agitation
(30 mL of IRN 150 Resin with 50 Ci/m^3 C-14 loading)

RUN NO.	ACID CONC. (N)	ACID VOL. (mL)	REACTION TIME (min)	AGITATION SPEED (rpm)	C-14 RECOVERY (%)	REMARKS
R-1	3	480	90	30	90.3	Repeat of run 2-3
R-2	3	480	90	30	90.0	Repeat of run 2-3
R-3	3	480	90	60	92.5	Repeat of run 2-3 at high agitation speed
E-1	9	90	40	60	87.5	Based on prior test results of run 5-3
		120	90	60	87.5	Added acid and continued E-1 for 45 min
E-2	9	90	45	60	82.4	Repeat of E-1
E-3	6	135	45	60	100.7	Attempt E-2 with lower acid conc. but same total acid
		(180)	(90)	(60)	-	Designed to repeat S-2 by continuation of E3 but cancelled due to high recovery already obtained
			(135)	(60)	-	Further continuation of E-3 but cancelled due to high recovery already obtained
E-4	9	120	90	60	91.5	Increase acid and time of E-2 and repeat
E-5	6	135	45	60	99.1	Repeat E-3

Finally, run E-5 was conducted to repeat run E-3 which produced the best result, and the high recovery efficiency was approximately reproduced at 99.1%. It is therefore feasible to achieve practically complete recovery of C-14 from spent resins by agitating the resin with HCl. One set of operating conditions have been established by two repeated experimental runs that yielded recovery efficiencies between 99-100%. In the next section, the reproducibility of these results will be examined.

3.3 Experimental Reproducibility

Ten runs were performed under experimental conditions similar to those of run E-3 to determine the reproducibility of the efficient recoveries demonstrated by the previous runs E-3 and E-5. The experimental conditions employed here were similar to those of run E-3 except that the batch size was reduced to 10 mL of resin instead of 30 mL to minimize isotope usage. The volume of acid used was 120 mL which was not reduced proportionately because a minimum volume was required to keep the magnetic stirrer and air sparger in the flask immersed. This relatively large volume of acid was not expected to affect the performance significantly since the amounts of acid used previously were already in large excess.

The results are summarized in Table 5, where the statistical parameters calculated from the results are also presented. The computed sample mean of C-14 recovery was 100.3% and the sample standard deviation was 1.3%. Based on these statistics, a Student-t test applied to the null hypothesis (Ho) that the true mean of C-14 recovery is 100% shows that the probability of committing a Type I error (ie, error of false rejection) is less than 1% (ie, 99% level of significance). Therefore, Ho shall not be rejected. To accept Ho, an alternative hypothesis (H_A) must be defined with a hypothesized alternative mean and a specific Type II error (ie, error of false acceptance). It can be shown that by relaxing the level of significance for Type I error to 95%; an alternative mean can be specified as 98.5% of C-14 recovery, and the probability of committing a Type II error in accepting the null hypothesis is less than 10%.

To state these statistical results more concisely, it can be claimed that the overall recovery of C-14 by the acid agitation method is between 98.5-100%. The probability of committing a Type I error in falsely rejecting this claim is less than 5% while that of committing a Type II error in accepting this claim is less than 10%.

The stripped resins from runs 2, 4 and 8 of Table 5 were analyzed for residual C-14 by total combustion of the resin and analyzing the off-gas, and the results were below the detection limit of 0.5 nCi/mL (ie, 0.5 mCi/m^3) in all cases. This accounted for only 0.001% of the C-14 originally loaded on the resin, and it can be inferred that the C-14 was practically completely removed from the resins. The discrepancies with the recovery efficiencies were probably attributable to the absorption inefficiencies, scintillation counting inaccuracies and experimental error.

The use of a batch reactor for agitating spent resin with acid has been demonstrated consistently as an effective method for removing C-14 from simulated spent resin, and the results are encouraging.

TABLE 5

Statistical Evaluation

Experimental Conditions

Resin Volume	= 10 mL of IRN 150
Acid Concentration	= 6 N HCl
Acid Volume	= 120 mL
Reaction Time	= 45 minutes
Agitation Speed	= 60 rpm

Results

Percent recovery of C-14 from simulated moderator spent resin (50 Ci/m^3 loading of $NaH^{14}CO_3$ on IRN 150 resin) in 10 Trials:

(1) 99.90% (2) 100.02% (3) 102.20% (4) 98.56% (5) 101.46%
(6) 99.36% (7) 100.31% (8) 102.65% (9) 99.34% (10) 99.70%

Statistical Tests

Mean recovery efficiency : $\bar{x} = 100.35\%$

Sample standard deviation: $S = 1.3285$

Null Hypothesis Ho: Recovery efficiency, $Uo = 100\%$
Alternative Hypothesis H_A: $Uo \neq 100\%$

Student-t Statistic : $T_9 = \frac{(\bar{x}-Uo)}{S/\sqrt{n}} = 0.833$

$t_{9,0.005} = 3.25$

Since $T_9 < t_{9,0.005}$, therefore do not reject Ho.

Additional laboratory experiments should be performed with actual spent resins, and further process development work on a pilot-plant scale is recommended.

3.4 Tests on Actual Spent Resin

Due to limited availability of samples, only one experiment was conducted with actual moderator spent resin from Bruce NGS (sample collected from Station A Unit 2 in Nov. '86) and the results are summarized in Table 6. The resin was first analyzed by total combustion for the C-14 content, and then about 10 mL of it was agitated with 480 mL of 6N HCl for 90 minutes. The C-14 in the off-gas was absorbed in 2N NaOH solution, and the total activity recovered in the solution was 499 μCi, amounting to about 52% of the total activity originally detected on the resin. It was suspected that the remaining amount of C-14 may be present on the resin in organic forms, and the acid-stripped resin was further treated with potassium persulfate. But no significant amount of C-14 could be further recovered. When the final sample of stripped resin was combusted and analyzed for residual C-14, only 12 nCi/mL was detected. Therefore, the removal of C-14 from the resin was essentially complete, but the recovery efficiency determined by measuring the activity in the absorbing solutions was poor. About 48% of the original activity on the resin was unaccounted for. No satisfactory explanation can be offered at present, except that the inaccuracies in the activity measurements and the difficulties in taking homogeneous and representative solid samples from the bulk of the spent resin may have contributed significantly to the overall discrepancy. Extra care should be exercised in future work.

The changes in gamma activity levels on the resin sample due to acid stripping were also monitored and the results are summarized in Table 6. Neglecting the activities measured with high uncertainties (larger than 20%), most of the radionuclides were effectively removed from the resin and retained in the acid solution. The removal efficiencies of these nuclides by acid stripping ranged from 81 to 97% with the exception of Nb-95, for which the removal efficiency was only 44%. The discrepancy in the activity balance of these species ranged from 2 to 43%.

The significance of the above results from one single experiment should not be over-emphasized, and continued laboratory tests with actual spent resins are required.

4.0 OFF-GAS SORBENTS AND ACID WASTES

The performance of the liquid absorbent, NaOH, for removing $^{14}CO_2$ from the off-gas has been satisfactory, but the use of a solid sorbent such as $Ca(OH)_2$ proposed by Cheh et al/11/ may offer advantages in being more readily disposable.

Three experiments (runs S-1, S-2 and S-3) were conducted with $Ca(OH)_2$ solid sorbent and the results are presented in Table 7. It can be seen from the results that the $^{14}CO_2$ was effectively removed, but the utilization of the

TABLE 6

TOTAL ACTIVITY BALANCE
(SAMPLE SIZE = 7 gm, or 10 mL OF BRUCE UNIT 2 NOV. '86 MODERATOR SPENT RESIN)

	BEFORE STRIPPING		AFTER STRIPPING						
	RESIN		RESIN		SOLUTION				
ISOTOPE	TOTAL ACTIVITY (μCi)	PERCENT UNCERTAINTY (%)	ACTIVITY ON RESIN (μCi)	PERCENT UNCERTAINTY (%)	ACTIVITY IN SOLUTION (μCi)	PERCENT UNCERTAINTY (%)	PERCENT[1] ACTIVITY REMOVAL (%)	TOTAL ACTIVITY (μCi)	TOTAL[4] ACTIVITY DISCREPANCY (%)
Beta Activity:									
C-14	964.2	-	0.1	-	499.0[2]	-	99.9	499.1	48.2
Gamma Activity:									
Co-60	219.0	6.8	10.7	6.9	180.0[3]	6.9	95.1	190.7	12.9
Cr-51	3.2	81.9	---		---		---	---	---
Cs-137	2.8	17.0	0.1	18.6	2.1	18.7	96.4	2.2	2.0
Ce-144	13.6	13.3	1.7	10.0	9.7	17.2	87.5	11.4	12.8
Eu-152	5.2	18.6	0.6	8.4	3.8	15.7	88.5	4.4	4.3
Gd-153	572.3	11.1	45.9	8.5	303.1	10.4	92.0	349.0	39.0
Fe-59	0.9	52.1	0.2	14.8	---	---	77.8	0.2	77.8
Ru-106	6.4	23.0	1.4	12.3	3.0	79.5	78.1	4.4	31.3
Mn-54	30.5	7.0	0.9	7.2	24.3	7.1	97.0	25.2	17.4
Nb-95	5.7	10.1	3.2	7.0	1.0	27.9	43.9	4.2	26.3
Tb-160	17.6	15.2	3.3	8.0	6.8	15.6	81.3	10.1	42.6
Zn-65	3.0	46.9	0.9	8.0	---		70.0	0.9	70.0
Zr-95	2.8	33.1	---	8.1	0.8	62.5	---	0.8	71.4
Sc-46	1.0	72.9	0.4	8.1	---		60.0	0.4	60.0
Sb-125	1.6	59.2	0.4	12.2	1.0	58.7	75.0	1.4	12.5
Sn-113	0.5	72.7	---		0.4	75.2	---	0.4	20.0

1 Calculation is based on activities measured on resin after stripping, since these measurements generally indicated less percent uncertainty than those for the stripping solution.

2 Retained in NaOH absorbing solution.

3 Retained in HCl stripping solution.

4 Percent of original total activity unaccounted for in the total activity balance after acid stripping.

TABLE 7

OFF-GAS REMOVAL BY SOLIDS ADSORBENTS
(IRN 150 RESIN LOADED WITH 50 μC/mL OF $NaH^{14}CO_3$

					88.6% PURE $Ca(OH_2)$ SOLIDS COLUMN				
					FIRST COLUMN		SECOND COLUMN		
RUN NO.	ACID CONCENTRATION (N)	RUN TIME (Min)	AGITATION SPEED (*)	ACID VOLUME (mL)	AMOUNT OF SORBENT (gm)	ACTIVITY REMOVED (μCi)	AMOUNT OF SORBENT (gm)	ACTIVITY REMOVED (μCi)	PERCENTAGE C-14 RECOVERY (%)
S-1	3	90	High	180	20	1,632	10	0	95.6
S-2	6	90	High	180	15	1,643	5	0.3	96.3
S-3	9	90	High	120	15	1,673	5	0.2	98.1

* The "high" speed corresponds to approximately 60 rpm of magnetic stirring.

sorbent was low (eg, about 1% is estimated for the first trap in run S-1). It should be pointed out that the primary objective of these preliminary experiments was to remove and account for all the C-14, and that the sorbent columns were conservatively sized to maintain zero-breakthrough conditions. If a higher breakthrough such as 5-10% of inlet concentration (which would be permissible if the carrier gas is recycled) is permitted and a slower gas velocity is used the utilization can be improved up to 80% as reported by Cheh et al/11/.

To assess the production of spent sorbent as waste by-product, the following estimates can be used for an average sample of moderator spent resin with an activity level of 50 Ci/m^3: (1) the concentration of the radioactive carbonate will be about 0.0015 meq/mL of resin, estimated from the specific activity of C-14; (2) the concentration of the non-radioactive carbonate will be about 0.2 meq/mL resin, based on results of separate experiments using resins containing no active C-14. The amounts of 2N NaOH solution and $Ca(OH)_2$ solids (assuming 88.6% pure) required to remove all the carbon dioxide in the off-gas streams are estimated to be 20 mL and 24 mL per 100 mL of resin treated respectively. The utilization of the sorbents are based on a concentration reduction from 2N to 1N for the NaOH solution, and on 80% utilization for the $Ca(OH)_2$ solids.

The production of liquid sorbent waste appears to be less in volume, but the ultimate disposal will require immobilization, which increases the final volume. The volume reduction aspects of the secondary wastes will have to be assessed in greater detail when the type of sorbent (NaOH solution vs $Ca(OH)_2$ solids) is selected and the post treatment of the wastes is better defined.

The ultimate disposal of the spent acid, which will be contaminated by gamma radiation from the metal cations removed from the resin, also requires careful consideration. Stoichiometrically, about 0.02 equivalent of acid is required for each 100 mL of resin processed. If the acid concentration is reduced from 6N to 4N during processing, the acid waste production would be about 10 mL per 100 mL resin, but this waste production can be further reduced by recycling the spent acid.

Spent acid may be recycled by either: (1) removing the radioactivity from the acid after each batch operation and reusing the acid with proper concentration adjustment; or 2) recycling the acid after each batch operation with fresh acid make-up until the build-up of activity level reaches a predetermined maximum. The ultimate disposal will probably require steps of neutralization, precipitation and filtration.

Collectively for the off-gas sorbent and the spent acid, it is estimated that about 30 mL of radioactive waste (liquid and/or solids) will be generated per 100 mL of resin treated. Possibilities for further volume reductions as well as means for ultimate waste disposal will have to be studied in greater detail.

5.0 CONCLUSIONS AND RECOMMENDATIONS

1. Based on experimental results with simulated spent resin, the method of acid stripping in an agitated batch reactor is seen to be a simple and efficient method of removing C-14 from spent resin.

2. A C-14 recovery of 98.5-100% can be claimed for the method of acid agitation with the following levels of statistical significance: the probability of committing a false rejection would be less than 5% and the probability of committing a false acceptance would be less than 10%.

3. Three acid-stripped resin samples were analyzed and no appreciable residual C-14 was found in all cases. The efficiency of removing C-14 from the resin was probably better than that indicated by the recovery measurements.

4. Only one experiment with actual spent resin was performed. About 52% of the measured C-14 was recovered in the absorbing solution, but the acid-stripped resin was analyzed to be free of residual C-14 indicating that the removal of C-14 from resin should be nearly 100%. The activity balance was not satisfactory.

5. Preliminary assessment indicates that about 30 mL of secondary wastes would be generated per 100 mL of spent resin treated.

6. The following areas are recommended for further developmental work: (1) laboratory evaluation with actual spent resin, (2) more detailed assessment of secondary waste generation and disposal, and (3) process evaluation on a pilot-plant scale.

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APPENDIX A - PREVIOUS RESULTS

(Ref: B.R. Nott, Int. J. Appl. Radiat. Isot. Vol. 33, pp. 584-585, 1982)

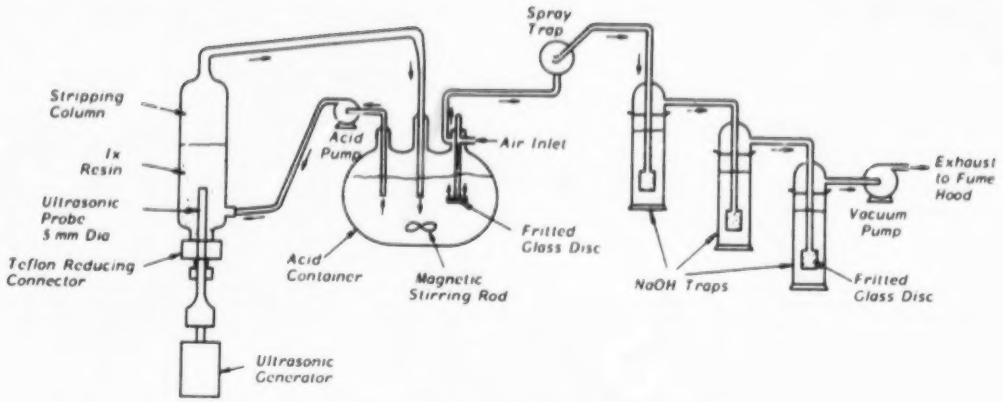

Fig.A Acid stripping apparatus for ^{14}C determination.

Table A Results of acid stripping runs for ^{14}C removal from ion exchange resins

Run number	Acid concentration (mol/l)	Acid volume (ml)	Acid circulation rate (ml/min)	Run time (min)	Peak ultrasonic power (W)	Ultrasonic power on–off cycle time (s–s)	NaOH concentration in traps (mol/l)	Percentage ^{14}C recovery
1	2.0	360	50	45	40	10–50	2.0	91.8
2	3.0	360	50	90	20	5–55	2.0	99.8
3	2.0	480	50	90	20	10–50	0.5	96.4
4	3.0	480	50	45	40	5–55	0.5	97.7
5	2.0	360	90	90	40	5–55	0.5	102.1
6	3.0	360	90	45	20	10–50	0.5	98.2
7	2.0	480	90	45	20	5–55	2.0	92.8
8	3.0	480	90	90	40	10–50	2.0	100.1

APPENDIX B

PRELIMINARY RESULTS

TABLE B-1

Preliminary Results For Simulated Moderator Spent Resin
(30 mL IRN 150 Resin at 50 μCi/mL Loaded with $NaH^{14}CO_3$

Run No.	Acid Concentration (N)	Acid Volume (mL)	Run Time (min)	Agitation Speed (*)	Percentage C-14 Recovery
P-1	3	360	45	high	90.5
P-2	3	480	45	low	149.6
P-3	3	480	45	low	82.8
P-4	3	360	90	high	98.1
P-5	2	360	45	low	111.5

* "low" and "high" speeds correspond to approximately 30 and 60 rpm of magnetic stirrings respectively.

TABLE B-2

Preliminary Results For Simulated PHT Spent Resin
(30 mL IRN 154 Resin with 5 μCi/mL Loading

Run No.	Acid Concentration (N)	Run Time (min)	Agitation Speed (*)	Acid Volume (mL)	Percentage C-14 Recovery	Source of Activity
P-6	3	45	high	360	118.7	$NaH^{14}CO_3$
P-7	3	45	high	360	102.4	$NaH^{14}CO_3$
P-8	3	45	low	480	103.0	$NaH^{14}CO_3$
P-9	3	90	low	480	109.4	$NaH^{14}CO_3$
P-10	3	90	high	360	113.5	$NaH^{14}CO_3$
P-11	1	90	high	480	98.7	$NaH^{14}CO_3$
P-12	1	45	high	480	109.8	$NaH^{14}CO_3$
P-13	1	90	low	360	112.1	$NaH^{14}CO_3$
P-14	1	45	low	360	98.1	$NaH^{14}CO_3$
P-15	1	45	low	360	116.1	$Na_2{}^{14}CO_3$
P-16	3	45	high	360	84.9	$Na_2{}^{14}CO_3$
P-17	3	90	low	480	102.3	$Na_2{}^{14}CO_3$

* "low" and "high" speeds correspond to approximately 30 and 60 rpm of the magnetic stirrer respectively.